Can Humic Substances Alter Fertilizer Reaction Pathways in Acid Soils?

Joseph J. Weeks and Dr. Ganga M. Hettiarachchi

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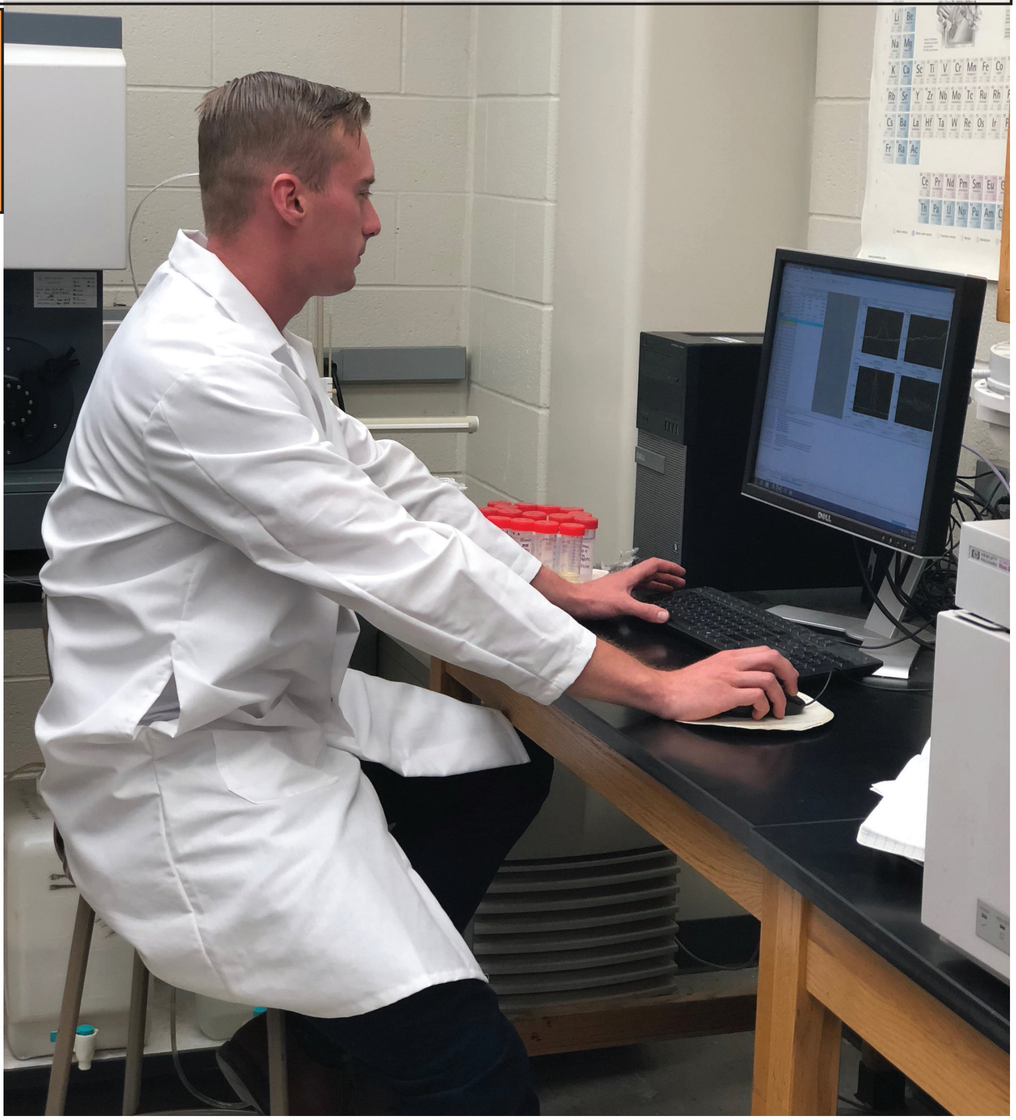
Summary: *Growers on acid soils may benefit from applying orthophosphate-based fertilizers rather than polyphosphates, if fluid P is to be used.*



Farmers will adopt more environmentally friendly phosphorus (P) management strategies when the fertilizer industry is able to supply economically viable, commercial products that reliably lower total P application rates without compromising crop productivity. Until then, barring increased governmental regulation, expecting farmers to institute practices that possess the potential to hurt their bottom line is nothing short of delusional.

Acid soils, which constitute more than 50% of global arable land, pose a formidable challenge to those working to improve plant P acquisition efficiency (Zheng 2010). Phosphorus fertilizer reaction chemistry in these soils is highly nuanced and complex. Factors such as iron and aluminum mineralogy, P fertilizer formulation, and pH, all govern P fate and transport. Thus, any solution that significantly improves P acquisition efficiency will need to address the many contributors to P fixation (Ainsworth et al. 1985, Hashimoto et. al. 1969).

One of the more controversial fertilizer enhancement products that frequently receives attention are the humic substances. Currently, growers and scientists are working to parse if these products are working, exactly how (Lyons and Genc 2016). One possible explanation is that the high cation exchange capacity associated with many of these substances could be blocking P fixation reactions with iron and aluminum in acid soils or calcium in calcareous soils (Lyons and Genc 2016). Degryse et al. (2013), however, concluded that this mechanism to block phosphorus fixation was likely not viable, though humic substances were not specifically vetted. If cation sequestration is not the mechanism, others including stimulation of soil microbiota and plant hormonal interactions are also plausible (Calvo et al. 2014). This study evaluated the impact of co-application of four commercial fulvic acid (FA) products with common liquid fertilizers on P lability in an oxisol from Brazil.

Methodology

Experimental Design. Sixty-three Petri dishes (88mm diameter and 12.9 mm height) were packed to a bulk density of 1.1g cm-3 with an acidic, sand clay loam from São Paulo, Brazil (see Table 1) that had been prewetted to 18% maximum water holding capacity (MWHC). After packing, the soils were adjusted to 50% MWHC, the covers were replaced, the edges were wrapped in Parafilm, and the dishes were allowed to equilibrate at room temperature (~24°C) for at least 24 hours. Treatments were then slowly administered to the exact

Table 1. Select properties of the experimental soil.

Orgin	Classification	Texture	pH	$CaCO_3$	CEC	Total P	Oxalate Extractable Fe	Ozalate Extractable Al
			(1:10)	%	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Brazil	Typic Haplustults	SCL	5.4	-	4.25	206	1565	666

center of the dish using a 1 ml syringe. The application target rate was defined as enough fertilizer to equal 9.2 mg P dissolved in 125µL of E-pure water. Treatments consisted of a water-only control, technical grade monoammonium phosphate (MAP) (FisherBrand ACS Grade), technical-grade diammonium phosphate (DAP)(FisherBrand ACS Grade), ammonium polyphosphate (APP) (11-37-0 Mosaic formulation), and an 80/20 blend of MAP and APP (80/20), respectively, all with and without three commercial humic substances: two labeled solely as fulvic acids (FA1 and FA2) and one as a blend of fulvic acid sub-fractions (SF FA). Additionally, a standalone phosphoric acid/sub-fraction of fulvic acid blend (PA/SF FA) was included as well. Following treatment administration, Parafilm was again employed to seal edges and mitigate moisture loss. The dishes were wrapped in aluminum foil to prevent light exposure and incubated for four weeks in the dark at 25oC. Following incubation, the dishes were excavated into four concentric circular sections with radii of 0-8mm, 8-15mm, 15.5-27mm and 27mm- dish edge extending from the point of application (POA). The sections were then dried at 40oC, weighed and finely ground with a mortar and pestle.

Chemical Analysis. Plant available P was assessed using the anion exchange resin technique followed by colorimetic analysis for the molybdate reactive (i.e. orthophosphate) fraction (Murphy and Riley 1962, Myers et al. 2005), and total P was determined by aqua regia digestion with subsequent ICP-OES analysis (Varian 720-ES) (Premarathna et al. 2010). Oxalate extractable (amorphous) iron (Fe) and oxalate extractable aluminum (Al) were analyzed according to Locppert and Inskeep (1996), and pH was assessed using an electrode in a 1:10 soil water suspension.

Results

pH. In general, treatment impact on soil acidity was attributed more to the P speciation in the fertilizer than co-application of fulvic substances. Most applications raised the pH at the POA. The sole exception was the P acid/sub-fraction of fulvic acid blend that significantly reduced the pH in the center two sections. This is likely due to the acidic nature of phosphoric acid. Absent any neutralizing agents or strong buffering capacity in the soil, addition of a concentrated acid would result in further acidification. Increased pH, relative to the control, was most pronounced in the DAP treatments (Figure 1). The PKa of the transition between diprotonated and monoprotonated P anion is 7.2, therefore when the monoprotonated anion is added to the acid soil, H+ is scavenged, reducing the proton concentration in soil solution, raising the pH. In addition, P chemisorption on oxyhydroxide surfaces releases hydroxyl groups to solution that complex with protons to form water, explaining why even the diprotonated P anions (e.g. MAP) elevated the pH.

% of P Added. The soil possessed a sandy clay loam texture that allowed for substantial P movement away from the POA (Figure 2). Although not statistically significant, orthophosphate treatments appeared to diffuse slightly further than polyphosphate treatments, and the phosphoric acid / sub-fraction of fulvic acid blend was the least mobile. In regards to the latter, pH reduction at the POA may explain this behavior, because P fixation on iron and aluminum oxyhydroxides as well as precipitation of iron or aluminum phosphates both positively correlate with rapid acidification. No FA addition effect can be definitively concluded at this time.

Resin Extractable P. Co-application of FA did not reliably improve lability as assessed by resin extractability after four weeks (Figure 3). Although the exact reason is currently uncertain, one proposed

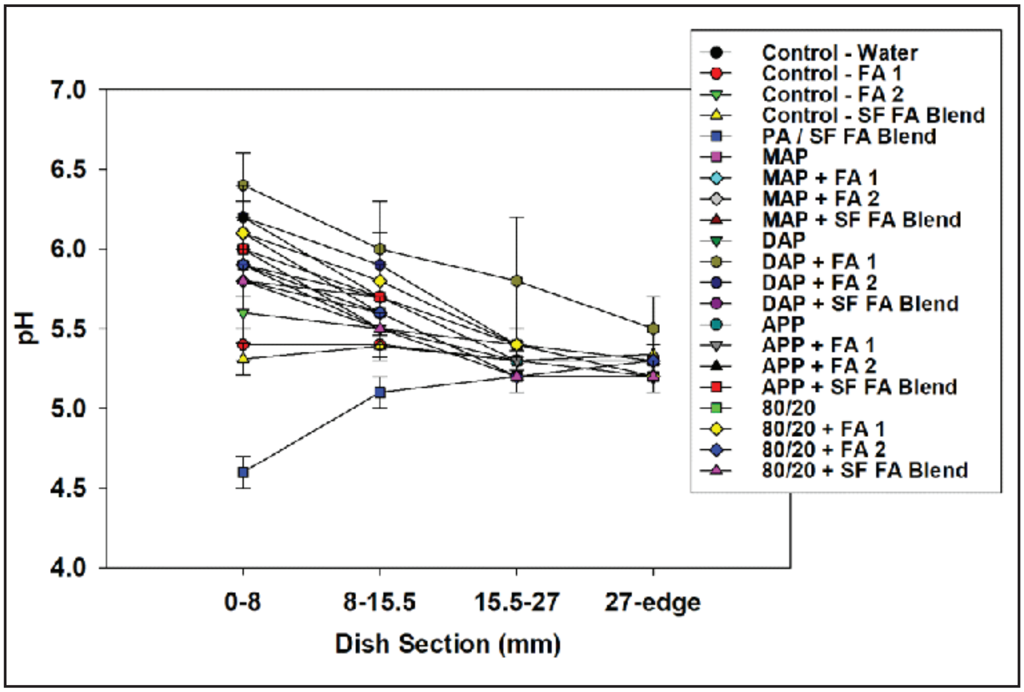


Figure 1. Brazilian soil pH by dish section.

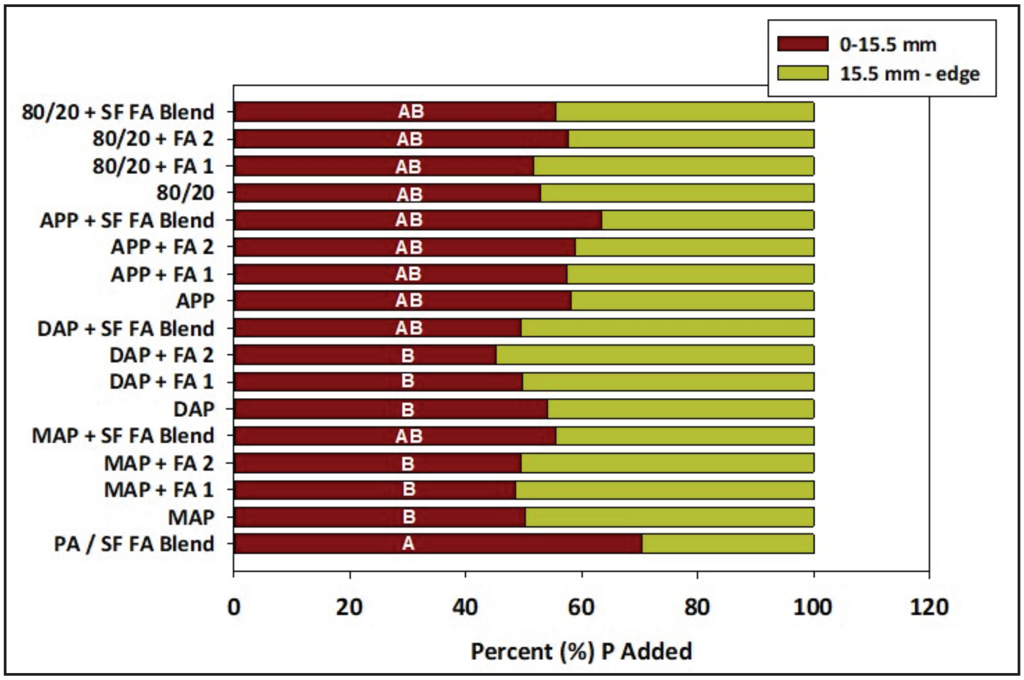


Figure 2. Diffusion of P from the POA by section expressed as a percent of total P added.

theory is that exchange sites on the organic acids were simply overwhelmed. Since the product is only applied at a rate of 0.73µL (FA 1), 0.78µL (SF FA) or 1.43µL (FA 2) per 125µL treatment, it is likely that more fixing cations and P sorption sites reside in the impacted soil volume than the fulvate can guard P from (Degryse et al. 2013). Additionally, under acidic conditions negatively charged functional groups are protonated more often compared to neutral or alkaline soil, resulting in an overall reduction in cation sequestration efficacy.

MAP and DAP performed superior to the APP and 80/20 treatments in the center sections, as is consistent with the findings of Hashimoto et al. (1969). This may be due to the greater affinity that polyphosphates have for iron and aluminum compared to orthophosphates. Despite its relative lack of mobility, the phosphoric acid / sub-fraction of fulvic acid blend results were similar to all other treatments when the labile fraction is compared against the total P added in each section.

Oxalate Extractable Iron an Aluminum at the POA. Addition of fertilizer to the soil appears to have slightly elevated the concentrations of amorphous iron and aluminum as compared to controls (Figure 4). The only treatment to differ from the rest however was the phosphoric acid / sub-fraction of fulvic acid blend. Because this product is so acidic and reduced the pH in the center section, more stable iron and aluminum minerals probably dissolved at the POA. A fraction of the released Fe and Al likely reprecipitated as amorphous minerals, while some would have remained in soil solution. Both fractions would have been extracted in this procedure. Sorption of P to the newly formed amorphous iron and aluminum minerals and possible physical occlusion during the reprecipitation process help to explain why, for this treatment, P did not diffuse as far as the others.

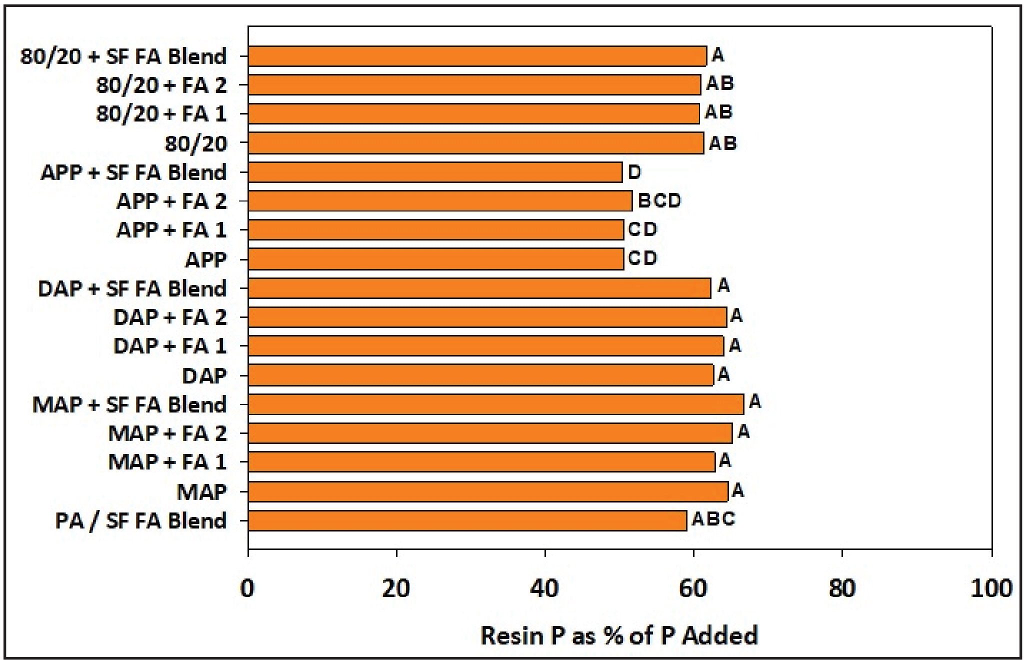


Figure 3. Resin extractable P presented as a percent of the total P added in the 0-15.5mm section.

Summing Up

Fulvic acid addition to liquid P in this study did not seem to significantly improve P lability. The reason may be due to insufficient application rate or simply that the mechanism by which these products improve yield is not through inhibition of fixation. Differences were observed between types of fertilizers. Growers on acid soils may benefit from applying orthophosphate-based fertilizers, rather than polyphosphates, if liquid P is to be used.

Dr. Hettiarachchi is a Professor and J. Weeks is a PhD Candidate of Soil & Environmental Chemistry at the Throckmorton Plant Sciences Center, Kansas State University in Manhattan Kansas

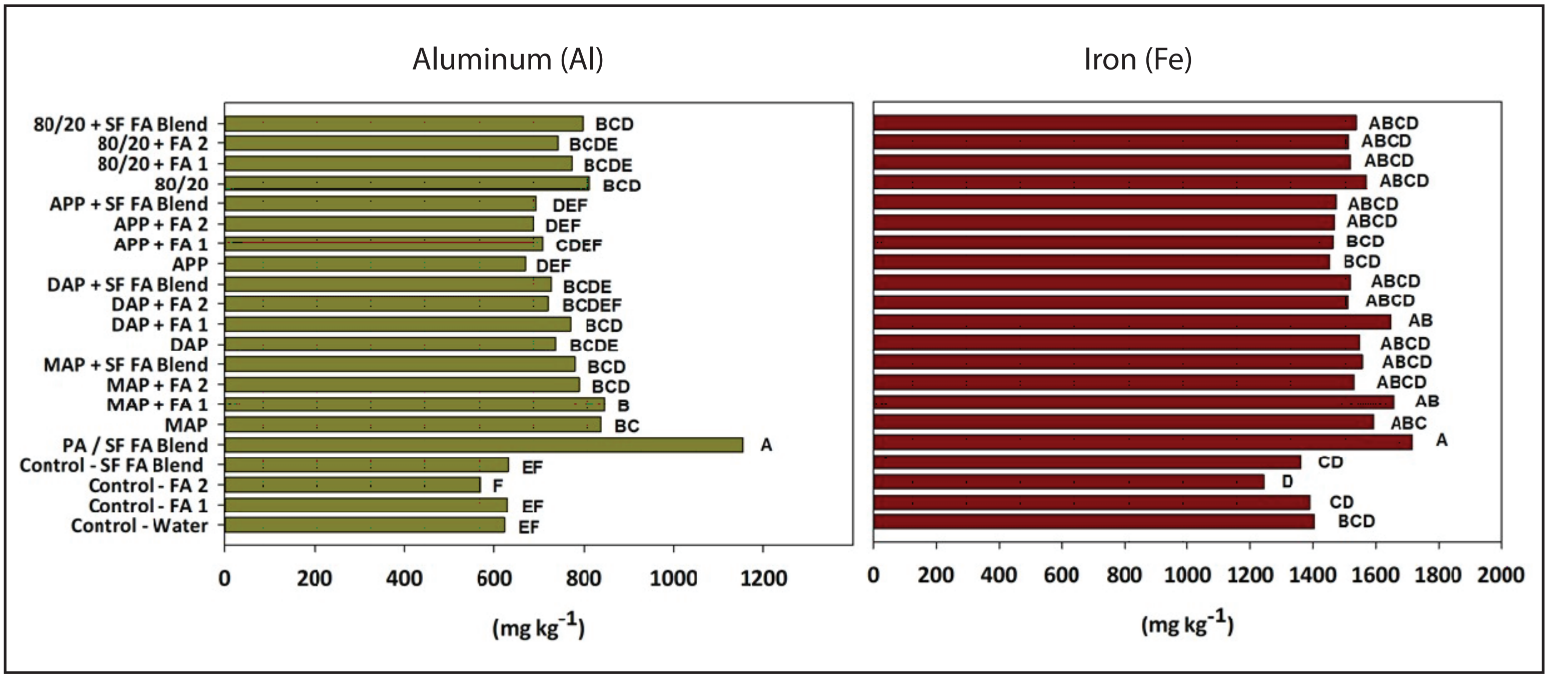


Figure 4. Oxalate extractable iron and aluminum in the center dish section (0-8mm)